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(54) Title: PROCESS FOR PREPARING SILICONE ELASTOMER COMPOSITIONS

(57) Abstract

A process is provided for preparing a silicone elastomer composition for cosmetic products which includes the steps of feeding the silicone elastomer composition comprising a silicone rubber in a carrier fluid into a reactor, mixing the composition in the reactor, delivering the composition from the reactor into a high pressure pump, pumping the fluid into a device for reducing particles of rubber into smaller sizes and recirculating the resultant size reduced particles back to the reactor. The device for reducing particle size is preferably a high pressure fed homogenizer, most advantageously a sonolator.

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PROCESS FOR PREPARING SILICONE ELASTOMER COMPOSITIONS

BACKGROUND OF THE INVENTION

Field of the Invention

The invention concerns a process for preparing cosmetic

products or work-in-progress components of such products
which include silicone elastomers as a functional
ingredient.

The Related Art

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Over the last four decades a rich variety of silicone materials have been commercialized for use in cosmetics. Although expensive, silicones have many unusual properties rendering them almost indispensable for certain types of products. Lubricity, compatibility, stability, dispersibility, thickening ability and other properties have been deemed quite valuable.

Among the multitude of silicone materials, the rubber-like
25 polysiloxane elastomers have received attention as
components in both aqueous emulsions and nonaqueous
formulations. Illustrative of the art is WO 96/18374 (Estee
Lauder) describing a stable water-in-oil emulsion
incorporating an organopolysiloxane elastomer having a
30 degree of cross-linking sufficient to provide a rubber-like
material. A skin treatment cream was exemplified employing
Gransil, a mixture of octamethylcyclotetrasiloxane and
organopolysiloxane rubber. The components were formulated
as three phases which were homogenized with a Silverson

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Homogenizer. In a second example, a cosmetic foundation was prepared through a combination of low and high shear mixing.

- U.S. Patent 4,983,418 (Murphy et al.) discloses hair spray compositions which include a silicone gum which when applied to hair imparts style, retention and conditioning benefits. Diphenyl-dimethyl polysiloxane gum is reported to be the preferred embodiment.
- 10 U.S. Patent 5,266,321 (Shukuzaki et al.) describes oily make-up cosmetic compositions normally in solid form. These compositions contain a silicone gel which includes a partially crosslinked organopolysiloxane polymeric compound and a low viscosity silicone oil. The polymeric compound is preferably prepared by the addition polymerization of an organo-hydrogen polysiloxane and an organopolysiloxane having unsaturated aliphatic groups. Solid foundations described in the examples are prepared in a step including homogenization in a triple roll mill.
- U.S. Patent 4,980,167 (Harashama et al.) reports cosmetic compositions exhibiting lubricancy derived from a silicone rubber powder ingredient within a silicone oil. A preferred rubber derives from the addition reaction between an organopolysiloxane containing at least two vinyl groups, an organopolysiloxane containing at least two silicon bonded hydrogen atoms and a platinum catalyst. Oily foundations, lipsticks and moisturizing creams are exemplified. Related silicone rubbers are reported in U.S. Patent 4,742,142

 (Shimizu et al.). This patent focuses upon synthesis of the rubber.

Although of great potential, the silicone elastomer materials commercially available or even hitherto reported

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in the literature have physical properties insufficiently suitable for elegant cosmetic products.

Accordingly, it is an object of the present invention to

5 provide a process for preparation of silicone elastomer
compositions containing a silicone rubber within a carrier
fluid, the process converting the rubber to a form stably
dispersed in the carrier fluid and exhibiting a silky
skinfeel when combined into cosmetic products.

These and other objects of the present invention will become more apparent from the following summary and description.

SUMMARY OF THE INVENTION

According to a first aspect, the present invention provides a process for reducing the particle size of the silicone elastomer within a silicone elastomer composition comprising silicone elastomer in a carrier fluid, said process comprising putting the silicone elastomer composition through a high pressure homogeniser whereby the elastomer particle structure is broken down.

In a second aspect, the present invention provides a process
for reducing the particle size of the silicone elastomer
within a silicone elastomer composition comprising silicone
elastomer in a carrier fluid, said process comprising
forcing the silicone elastomer composition under pressure,
preferably high pressure, through a means comprising a small
orifice or gap whereby the elastomer particle structure is
broken down.

The process of this invention is not directed at synthesis of any silicone elastomer as such but rather concerns a method to physically manipulate a pre-synthesized elastomer

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into a form more suitable for certain cosmetic products and in particular into a form that may facilitate the processing of such silicone elastomer compositions in cosmetic products. Transformations of the present invention are intended to customize elastomer particle sizes and composition viscosities to match requirements for the cosmetic product.

The silicone elastomer for use in the process of the present invention is preferably a crosslinked non-emulsifying siloxane elastomer formed from a divinyl monomer reacting with Si-H linkages of a siloxane backbone. A volatile siloxane such as cyclomethicones is the preferred carrier fluid for delivery of the elastomer through the recirculating system.

Thus, according to a third aspect, the present provides a process for preparing silicone elastomer compositions for use in cosmetic products which compositions comprise a silicone elastomer within a carrier fluid, the process including the steps of:

- (i) feeding a silicone elastomer composition comprising a silicone elastomer and a carrier fluid into a reactor;
- (ii) mixing the silicone elastomer composition through agitation in the reactor;
- (iv) pumping the agitated silicone elastomer composition from the high pressure pump into a means for reducing the silicone elastomer within the composition into a smaller particle size; and

- (v) optionally, recirculating the resultant smaller sized silicone elastomer particles into the reactor.
- The means for reducing particle size may be a special variety of homogenizer wherein under pressure the silicone composition is forced through a small orifice with high local energy applied to breakdown particle structure of the silicone elastomer. A particularly preferred device is a sonolator operating with an ultrasonic blade which generates turbulent cavitation bursts.

In a fourth aspect, the present invention provides for a silicone elastomer composition comprising a silicone rubber within a carrier fluid, the rubber having an average particle size ranging from 0.5 to 30 micron.

According to a further aspect of the invention, there is provided an antiperspirant or deodorant composition for topical application comprising:

- (i) an antiperspirant or deodorant active;
- (ii) volatile silicone; and
- (iii) a silicone elastomer composition,

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characterised in that the silicone elastomer composition is prepared according to the process of the invention.

BRIEF DESCRIPTION OF THE DRAWING

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The process of the present invention will now be described by way of example only, with reference to the following drawing in which figure 1 shows a schematic drawing of

according to the present invention a preferred embodiment of the process according to the present invention.

DETAILED DESCRIPTION OF THE INVENTION

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Now it has been discovered that silicone elastomers can be prepared for use with cosmetic products in a procedure which reduces their particle size by repeated treatment in a highpressure fed homogenizer. Figure 1 illustrates a preferred embodiment. Therein a silicone elastomer dispersed within cyclomethicone carrier at an elastomer concentration of from 1 to 95%, preferably from 5 to 30%, optimally from 15 to 20% by weight of the silicone elastomer/cyclomethicone composition, is charged to a reactor 2 as a silicone elastomer composition. Additional cyclomethicone carrier in an amount from 0 to 95%, preferably from 50 to 80%, optimally from 65 to 75% by weight based on the amount of final recirculated elastomer composition may be charged to the reactor through a separate feed line 4. The silicone 20 elastomer composition and any additional cyclomethicone carrier is then mixed by a slow speed counter-sweep mixer 6 to agitate the mixture.

Within reactor 2, is a high-shear homogenizer 8 employing a series of blades to produce high energy shear forces onto 25 the mixture. Homogenizer 8 improves the resultant product but is not a necessary element of the process. configurations, homogenizer 8 may be placed outside reactor 2 in a location prior to the high pressure pump 10.

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Upon completion of agitation in reactor 2, the resultant fluid mixture is delivered from the reactor into a feed pump The feed pump 9 is a positive displacement pump such as Waukesha PD gear pump. Thereafter the fluid mixture is transferred to a high pressure pump 10. Pressures generated

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by pump 10 may range from 500 to 40,000, preferably from 1,200 to 20,000, optimally from 1,800 to 10,000 psi. Typically, pump 10 may be a triplex plunger type available from the Giant Corporation, Toledo, Ohio or from the Cat Corporation.

Silicone elastomer composition under high pressure is then pumped into a type of homogenizer 12 requiring fluid to pass through a narrow orifice which reduces particle size. The preferred embodiment employs a sonolator available from the 10 Sonic Corp., a unit of General Signal. The sonolator is an in-line device capable of converting the kinetic energy of a high velocity stream of liquid into a high intensity mixing action. Conversion is accomplished by pumping the liquid through an orifice against a bladelike obstacle immediately 15 in the jet stream of the liquid. The liquid itself oscillates in a stable vortexing pattern, which in turn causes the blade-like obstacle to resonate, resulting in a high level of cavitation, turbulence and shear. The blade or knife is brought into an ultrasonic vibration by the 20 fluid motion, which causes cavitation in the fluid. cavitation (a phenomenon in which small gas bubbles in the fluid start to grow until they implode with very high local energy dissipation rates) then breaks up the droplet particles. U.S. Patent No. 3,176,964 to Cottell et al. 25 describes the sonolator in detail and its disclosure is hereby incorporated by reference.

Alternative high-pressure fed homogenizers other than the sonolator (preferred) are the Manton Gaulin type homogenizer available from the APV Manton Corporation and the Microfluidizer available from Microfluidics Corporation. These type of high pressure homogenizers contain a valve which is pressed (hydraulically or by a spring) against a fixed valve seat. Under high pressure, fluid flows through

the opening in the seat and then through a gap between the valve and seat. Although geometries of different high pressure homogenizers may differ in details, and may even be roughened with sharp edges, they all are generally similar. Often the high pressure homogenizer may consist of two or more valve-seat combinations.

Subsequent to high pressure homogenization, the silicone elastomer composition may, for best results, be recirculated into reactor 2. Recirculation according to the present 10 process normally ranges from 1 to 200 passes , preferably from 2 to 60 passes, optimally from 10 to 40 recycling passes. Temperatures within reactor 2 and throughout the system may range from 20 to 100°C, preferably from 35 to 60°C, optimally from 50 to 70°C. Silicone elastomer 15 particles resulting from the process will have an average particle size ranging from 0.05 to 30 micron, preferably from 0.2 to 10 micron, optimally from 0.5 to 5 micron. These particles are uniformly dispersed within the silicone oil (e.g. cyclomethicone) carrier. 20

Particle size may be measured using a Electro Zone Particle Sizing System (from Particle data Europe S.a.r.l.). In such a system, particles flowing nearly singly through a small liquid resistor cause a series of electrical pulses. The pulse amplitude represents the space occupied by a particle in the electrical field and thus allows the particle size to be measured.

30 Silicone elastomers of the present invention preferably are crosslinked non-emulsifying siloxane elastomers with average number molecular weights in excess of 10,000, preferably in excess of 1 million and optimally will range from 10,000 to 20 million. The term "non-emulsifying" defines a siloxane from which polyoxyalkylene units are absent. Advantageously

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the elastomers are formed from a divinyl monomer reacting with Si-H linkages of a siloxane backbone. Elastomer compositions are commercially available from the General Electric Company under product designation General Electric 5 Silicone 1229 named PolydimethylHydrogenSiloxane -Reaction Products with Vinyl Terminated Polydimethylsiloxane, delivered as 20-35% rubber in a cyclomethicone carrier. A related elastomer under the CTFA name of Crosslinked Stearyl Methyl Dimethyl Siloxane Copolymer is available as Gransil SR-CYC (25-35% active elastomer in cyclomethicone) from 10 Grant Industries, Inc., Elmwood Park, New Jersey. Amounts of the elastomer dispersed in the final cosmetic product formulated with the elastomeric composition derived from the process may range from 0.1 to 50%, preferably from 1 to 40%, more preferably from 3 to 20% by weight of the 15 final product.

The silicone elastomer may be dispersed within a silicone carrier. Illustrative of such silicone carriers are

20 silicone fluids such as the cyclo polydimethyl siloxane fluids of the formula [(CH,),SiO)], wherein x denotes an integer of from 3 to 6. The cyclic siloxanes will have a boiling point of less than 250°C and a viscosity at 25°C of less than 10 centipoise. Cyclomethicone is the common name of such materials. The tetramer and pentamer cyclomethicones are commercially available as DC 244 or 344 and DC 245 or 345 from the Dow Corning Corporation. Also useful is hexamethyldisiloxane available as DC 200 fluid (0.65 cs).

Hydrophobic carriers other than silicone fluids may also be employed as carriers. Petrolatum is the most preferred. Other hydrocarbons that may be employed include mineral oil, polyolefins such as polydecene, and paraffins such as isohexadecane (e.g. Permethyl 997 and Permethyl 1017).

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Compositions subject to the present method may either be anhydrous or contain water. When anhydrous, the amount of water will be confined to range from 0 to 5%, preferably not above 2%, optimally not above 0.5% by weight. When the compositions of this invention are in emulsion form, the amount of water will range from 5 to 50%, preferably from 7 to 30%, optimally from 10 to 20% by weight. The emulsions may be of the oil-in-water, water-in-oil or duplex variety. Aqueous to oily phases can range in weight from 10:1 to 1:10, preferably from 1:1 to 1:5, optimally from 1:1 to 1:2.

Hydrophillic carriers other than water may be present, such as polyhydric alcohols. Typical polyhydric alcohols include polyalkylene glycols and more preferably alkylene polyols and their derivatives. Illustrative are propylene glycol, dipropylene glycol, polypropylene glycol, polyethylene glycol, sorbitol, hydroxypropyl sorbitol, hexylene glycol, 1.3-butylene glycol, 1.2.6-hexanetriol, glycerin, ethoxylated glycerin, propoxylated glycerin and mixtures thereof. Most preferably the alcohol is glycerin. Amounts of alcohol may range anywhere from 1 to 50%, preferably from

10 to 40%, optimally from 25 to 35% by weight of the

cosmetic product .

Beyond the basic components, other materials may be included depending upon the particular type of cosmetic composition sought. For instance, surfactants may be formulated into the compositions. These may be selected from nonionic, anionic, cationic or amphoteric emulsifying agents. They may range in amount anywhere from about 0.1 to about 20% by weight. Illustrative nonionic surfactants are alkoxylated compounds based on C_{10} - C_{22} fatty alcohols and acids, and sorbitan. These materials are available, for instance, from the Shell Chemical Company under the Neodol trademark.

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Copolymers of polyoxypropylene-polyoxyethylene, sold by the BASF Corporation under the Pluronic trademark, are sometimes also useful. Alkyl polyglycosides available from the Henkel Corporation may also be utilized for purposes of this invention.

Anionic type surfactants include fatty acid soaps, sodium lauryl sulphate, sodium lauryl ether sulphate, sodium or magnesium glyceryl ether sulphonates, alkyl benzene sulphonate, mono- and di-alkyl acid phosphates and sodium fatty acyl isethionate.

Amphoteric surfactants include such materials as dialkylamine oxide and various types of betaines (such as cocoamidopropyl betaine).

Preservatives may be incorporated into the elastomer and cosmetic compositions of this invention to protect against the growth of potentially harmful microorganisms. While it is in the aqueous phase that microorganisms tend to grow, 20 microorganisms can also reside in the oil phase. As such, preservatives which have solubility in both water and oil are preferably employed in the present compositions. Suitable traditional preservatives are hydantoin derivatives, propionate salts, and a variety of quaternary 25 ammonium compounds. Cosmetic chemists are familiar with appropriate preservatives and routinely choose them to satisfy the preservative challenge test and to provide product stability. Particularly preferred preservatives are methyl paraben, propyl paraben, imidazolidinyl urea, sodium 30 dehydroxyacetate and benzyl alcohol. The preservatives should be selected having regard for the use of the composition and possible incompatibilities between the preservatives and other ingredients. Preservatives are

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preferably employed in amounts ranging from 0.01% to 2% by weight of the composition.

Minor adjunct ingredients may also be included such as fragrances, antifoam agents, opacifiers and colorants, each in their effective amounts to accomplish their respective functions.

Where the cosmetic composition is an antiperspirant

composition it is preferable that the antiperspirant active
is an astringent salt which combines the properties of
deodorancy and astringency. Suitable antiperspirant actives
are common in the art and include organic and inorganic
salts of aluminium, zirconium, zinc and mixtures thereof.

Preferably the antiperspirant active is present at levels of from 5 to 30% by weight of the cosmetic composition and more preferably from 15 to 30%.

- Where the cosmetic composition is a deodorant composition suitable deodorant actives include antimicrobials typically used as deodorant actives in the art, e.g. Triclosan, polyhexamethylene biguanide hydrochloride and ethanol.
- Where the cosmetic composition is an antiperspirant and/or deodorant composition, the silicone elastomer composition is typically present a levels of from 0.1 to 10% by weight of the cosmetic composition, preferably from 0.5 to 6% and more preferably from 2.0 to 4%.

The volatile silicone suitably comprises from 10 to 90% by weight of the cosmetic composition and preferably from 10 to 80% by weight.

The composition according to the invention can optionally comprise other ingredients, in addition to those already identified, depending on the nature and form of the finished product.

Examples of other ingredients which can optionally be present in a deodorant or antiperspirant composition according to the invention include emollients, such as non-volatile silicones, hydrocarbons or mineral oils.

Non-volatile silicones include polydimethylsiloxane having a viscosity in excess of 5 mm²s⁻¹, for example, from 50 to 1000 mm²s⁻¹, such as DOW CORNING 200 Fluids (standard viscosities 50-1000mm²s⁻¹).

Other useful emollients include PEG-400 distearate, and ethylene oxide and/or propylene oxide condensation products having the following formula:

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RO (C2H4O) a (C3H6O) bH

where R is either hydrogen or a hydrocarbon chain having from about 2 to 20 carbon atoms, and \underline{a} and \underline{b} are each from about 0 to 35 and $\underline{a} + \underline{b}$ is from about 5 to 35. One example of such an emollient is Fluid AP, a condensate of about 14 moles of propylene acid with about 1 mole of butyl alcohol sold by Union Carbide.

30 Still further emollients suitable for use in the present solid stick compositions include polyalphaolefins, e.g. polydecene, fatty acid and fatty alcohol esters and water insoluble ethers.

Where the cosmetic composition is an antiperspirant or deodorant composition, the composition may additionally comprise a masking oil, which can typically be present at a level of 3 to 40% by weight of the composition. Suitable masking oils include for example, polydecene, polybutene, ppg-14 butyl ether, non-volatile silicones, isopropyl myristate, isopropyl palmitate, C₁₂-C₁₅ alkyl benzoates, and mineral oils.

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Other optional ingredients include thickeners, such as clays, for example Bentone 38; and silica, for example Aerosil 200. However, in the present invention, preferred thickening agents are the silicone elastomer compositions.

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Other optional ingredients include skin feel improvers, such as talc and finely divided polyethylene, an example of which is ACUMIST B18; cosmetically acceptable vehicles, such as anhydrous ethanol and other emollients; perfumes; and preservatives.

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The composition according to the invention can take the form of a product suited to or adapted for topical application to human skin. Preferred product forms include soft solids, creams, lotions and sticks. In this respect, the cosmetic compositions may contain other cosmetic adjuncts conventionally employed in soft solid, cream, lotion or stick products, for example in deodorant or antiperspirant products.

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One convenient form of the composition according to the invention is a cream usually contained in a suitable holder or dispenser to enable it to be applied to the area of the

skin, particularly the underarm, where control of perspiration and deodorancy is required.

Solid products according to the invention may include a wax such as, castor wax, Synchrowax HRC, Carnaubau, beeswax, silicone waxes and glycerol monostearate and mixture thereof at levels of from about 1 to 10% preferably 2 to 8%. If present, the wax is believed to enhance structural stability of the composition in the molten state.

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The ingredients which can optionally be present in the cosmetic composition can conveniently form the balance of the composition.

The following examples will more fully illustrate the embodiments of this invention. All parts, percentages and proportions referred to herein and in the appended claims are by weight of the composition unless otherwise indicated.

EXAMPLE 1

This Example illustrates processing of a silicone elastomer composition into a work-in-progress constituent of a water-in-oil skin lotion. A 25 gallon reactor fitted in an upper area with a low shear counter-sweep mixing blade and in a lower area with a homogenizing blade was charged with the components listed in Table I.

10 TABLE I

Silicone Elastomer Composition

from 500 to 40,000 cps at 25°C.

| COMPONENTS | WEIGHT % |
|--|----------|
| General Electric Elastomer 1229 (25% elastomer solids in cyclomethicone) | 25 |
| Dow Corning 345 (cyclomethicone pentamer) | 45 |
| Dow Corning 244 (cyclomethicone tetramer) | 30 |

Temperatures throughout the process were maintained between 17 and 28°C. Under pressure the fluid blend of Table I was fed to a sonolator operating between 246 and 295 rpm maintaining a pressure between 2,800 and 3,500 psi.

20 Sonolated product was then returned to the reactor. A total of 19 passes recirculated fluid blend through the system. Resultant silicone elastomer composition exhibited a viscosity of 560 cps at 25°C with elastomer of particle size sufficiently small and dispersed within the cyclomethicone carrier to avoid any grainy feel. Viscosity measurements were taken on a Brookfield LV Viscometer (size 4 bar, 60 rpm, 15 sec.). Broad range of acceptable viscosity can vary

EXAMPLE 2

An essentially anhydrous final cosmetic product was prepared utilizing a silicone elastomer composition. The formulas are shown in Table II.

TABLE II

| COMPONENT | SILICONE ELASTOMER COMPOSITION (WEIGHT %) | FINAL COSMETIC PRODUCT (WEIGHT %) |
|--|---|--|
| General Electric Elastomer 1229 (34% elastomer solid in cyclomethicone) | 33.5 | 31.0 |
| Dow Corning 345 (cyclomethicone pentamer) | 45.4 | 42.0 |
| Dow Corning 344 (cyclomethicone tetramer) | 9.2 | 8.5 |
| Petrolatum (2.5 Hard) | 11.9 | 11.0 |
| Potassium Lactate (50% aqueous soln.) | 0.0 | 7.0 |
| Abil EM 90 (cetyl dimethicone copolyol) | 0.0 | 0.5 |

A 25 gallon reactor was charged with the silicone elastomer composition listed in Table II. Contents of the reactor were agitated with a Press-Industria mixer for a period of several minutes. A 25 DO Waukesha pump transferred the composition from the reactor to a high pressure pump operating at approximately 1,200 psi and thereafter into a sonolator (74-120 rpm). Sonolated fluid was then returned to the reactor and recycled through the system at flow rates ranging from 9 to 34 pounds per minute. Total process time

was 3 hours. The system was maintained at a temperature 54 to $62^{\circ}F$.

Sonolated fluid composition resulting from the process had a viscosity between 40,000 and 125,000 cps at 25°C measured on a Brookfield RTD (5 rpm heliopath spindle -30 sec). The composition was then combined with potassium lactate (50% solution) and a silicone copolyol (Abil EM 90) by agitation at a temperature between 37° to 60°F. The final cosmetic product formulation is listed in Table II.

CLAIMS

1. A process for reducing the particle size of the silicone elastomer within a silicone elastomer composition comprising silicone elastomer in a carrier fluid, said process comprising putting the silicone elastomer composition through a high pressure homogeniser whereby the elastomer particle structure is broken down.

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- 2. A process for reducing the particle size of the silicone elastomer within a silicone elastomer composition comprising silicone elastomer in a carrier fluid, said process comprising forcing the silicone elastomer composition under pressure, preferably high pressure, through a means comprising a small orifice whereby the elastomer particle structure is broken down.
- 20 3. A process for preparing silicone elastomer compositions for use in cosmetic products which compositions comprise a silicone elastomer within a carrier fluid, the process comprising the steps of:
- 25 (i) feeding a silicone elastomer composition comprising a silicone elastomer and a carrier fluid into a reactor;
 - (ii) mixing the silicone elastomer composition through agitation in the reactor;
- 30 (iii) transferring the agitated silicone elastomer composition from the reactor into a high pressure pump;
 - (iv) pumping the agitated silicone elastomer composition from the high pressure pump into a means for reducing the silicone rubber within

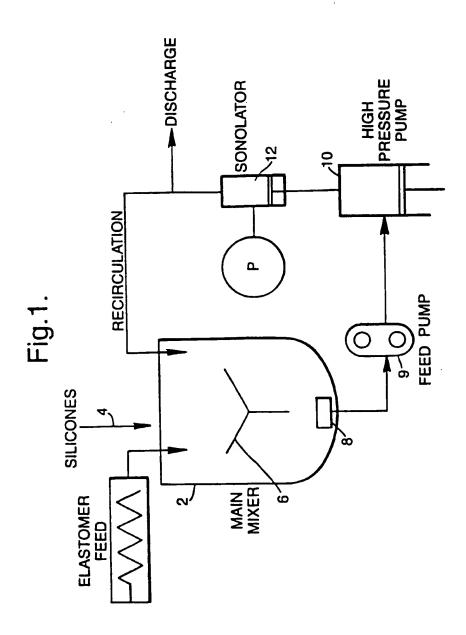
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- the composition into a smaller particle size; and
- (v) optionally, recirculating the resultant smaller sized silicone elastomer particles into the reactor.
- 4. The process according to claim 3 wherein the pumping is performed as a pressure ranging from 500 to 40,000 psi.
- 10 5. The process according to claim 4 wherein the pumping is performed at a pressure from 1,800 to 10,000 psi.
 - 6. The process according to any one of claims 2 to 4 wherein recycling between steps (ii) and (v) ranges from 1 to 200 passes.
 - 7. The process according to any preceding claim wherein temperature ranges from 20 to 100°C.
- 20 8. The process according to any one of claims 2 to 7 wherein the means is a homogenizer.
 - 9. The process according to claim 8 wherein the homogenizer is a sonolator.
- 10. The process according to any preceding claim wherein the silicone elastomer is dispersed within a silicone carrier.
- 30 11. The process according to any preceding claim wherein the silicone elastomer in the product of the process has an average particle size ranging from 0.05 to 30 micron.

- 12. The process according to claim 11 wherein the average particle size ranges from 0.5 to 5 micron.
- 13. The process according to any preceding claim wherein
 the silicone elastomer is a crosslinked non-emulsifying
 polysiloxane prepared from the reaction of a divinyl
 monomer and a Si-H siloxane.
- 14. The process according to any preceding claim wherein the carrier fluid is cyclomethicone.
 - 15. An silicone elastomer composition obtained by a process according to any one of claims 1 to 14.
- 15 16. A silicone elastomer composition comprising a silicone elastomer within a carrier fluid, the elastomer having an average particle size ranging from 0.05 to 30 micron.
- 20 17. The composition according to claim 16 wherein the silicone elastomer is a crosslinked non-emulsifying polysiloxane prepared from the reaction of a divinyl monomer and a Si-H siloxane.
- 25 18. The composition according to claim 16 or 17 wherein the carrier fluid is cyclomethicone.
 - 19. Cosmetic composition comprising:
- 30 (i) an antiperspirant or deodorant active;
 - (ii) volatile silicone; and
 - (iii) a silicone elastomer composition,

characterised in that the silicone elastomer composition is prepared according to any one of claims 1 to 14.



SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

ernational Application No PCT/GB 98/00828

A. CLASSIFICATION OF SUBJECT MATTER IPC 6 A61K7/48 A61K7/00 B01J2/18 C08L83/04 B29B9/00 B01J2/20

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols) IPC 6 A61K C08J B01J B29B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

| Category * | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|------------|--|-------------------------|
| , X | US 5 654 362 A (SCHULZ JR WILLIAM JAMES | 1-10, |
| | ET AL) 5 August 1997 | 13-15,19 |
| | see column 1, line 60-61 see column 2, line 6 | · |
| | see column 2, line 21 | |
| | see column 4, line 55 | |
| | see column 5, line 62-67 | |
| | | |
| X | EP 0 542 498 A (DOW CORNING) 19 May 1993 | 1-9, 11-13, 15-17 |
| | see page 4, line 37-47 | 15-17 |
| | see page 5, line 12-15 | |
| | see example 1 | |
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|--|---|
| * Special categories of cited documents : | T* later document published after the international filing date |
| "A" document defining the general state of the art which is not considered to be of particular relevance. | or priority date and not in conflict with the application but cled to understand the principle or theory underlying the invention |
| "E" earlier document but published on or after the international filing date | "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to |
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| which is cited to establish the publication date of another citation or other special reason (as specified) | "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the |
| "O" document referring to an oral disclosure, use, exhibition or other means. | document is combined with one or more other such docu- ments, such combination being obvious to a person skilled |
| "P" document published prior to the international filing date but later than the priority date claimed. | in the art "8" document member of the same patent family |
| Date of the actual completion of the international search | Date of mailing of the international search report |
| 24 August 1998 | 07/09/1998 |
| Name and making address of the ISA | Authorized officer |
| European Patent Office, P.B. 5818 Patentisan 2 NL - 2280 HV Rijswijk Tel. (-31-70) 340-2040, T.⊭. 31 851 epo nl, Fax: (+31-70) 340-3016 | Sierra Gonzalez, M |

Form PCT/ISA/210 (second sheet) (July 1992)

1

INTERNATIONAL SEARCH REPORT

PCT/GB 98/00828

| US 3 843 601 A (BRUNER L) 22 October 1974 1-3,13 |
|--|
| see column 1, line 29-30 see column 5, line 16-18 CHEMICAL ABSTRACTS, vol. 117, no. 10, 7 September 1992 Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| See column 5, line 16-18 CHEMICAL ABSTRACTS, vol. 117, no. 10, 7 September 1992 Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 See abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 See abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| CHEMICAL ABSTRACTS, vol. 117, no. 10, 7 September 1992 Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XPO02074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XPO02074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| 7 September 1992 Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| 7 September 1992 Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| Columbus, Ohio, US; abstract no. 91069, N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| N. TERAE: "Manufacture of siloxane microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 1-19 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| microemulsions by polymerization with ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 See abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| ultrasound" XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| XP002074429 see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 See abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| see abstract & JP 04 103 631 A (SHIN-ETSU CHEMICAL INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 See the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 See abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| INDUSTRY, CO., LTD.) 6 April 1992 US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| US 4 670 530 A (E. W. BECH) 2 June 1987 see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| see the whole document CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| CHEMICAL ABSTRACTS, vol. 108, no. 2, 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| 11 January 1988 Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| Columbus, Ohio, US; abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| abstract no. 6563, X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| X. ZHANG: "ultrasonic emulsion polymerization of siloxanes" XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| XP002074430 see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| see abstract & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| & HECHENG XIANGJIAO GONGYE, vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| vol. 10, no. 6, 1987, pages 418-422, Beijing (China) |
| Beijing (China) |
| GB 2 064 363 A (GEN ELECTRIC) 17 June 1981 1-19 |
| 1 GB 2 004 303 A (GEN ELECTRIC) 1/ JUNE 1981 1-19 |
| see the whole document |
| |
| A EP 0 279 641 A (UNILEVER PLC ;UNILEVER NV 1-19 |
| (NL)) 24 August 1988 |
| see the whole document |
| us 3 176 964 A (E. C. COTTELL) 6 April 1-19 |
| 1965 |
| cited in the application |
| see the whole document |
| K. EBERTH: "A comparative study of 1-19 |
| emulsions prepared by ultrasound and by a |
| conventional methol. Droplet size |
| measurements by means of a Coulter Counter |
| and microscopy" |
| INTERNATIONAL JOURNAL OF PHARMACEUTICS, |
| vol. 14, 1983, pages 349-353, XP002074428 see the whole document |
| The state of the s |
| |
| |

1

INTERNATIONAL SEARCH REPORT Information on patent family mombers

mational Application No PCT/GB 98/00828

| | ent document In search report | 1 | Publication date | | atent family member(s) | _ | Publication date |
|----|----------------------------------|---|------------------|------|---------------------------|-----|------------------|
| US | 5654362 | A | 05-08-1997 | NONE | | | |
| EP | 0542498 | Α | 19-05-1993 | CA | 2082749 | | 14-05-1993 |
| | | | | JP | 5222292 | ? A | 31-08-1993 |
| US | 3843601 | Α | 22-10-1974 | AT | 340139 | В | 25-11-1977 |
| | | | | AT | 817174 | A | 15-03-1977 |
| | | | | AU | 7248074 | A | 19-02-1976 |
| | | | | BE | 821012 | ? A | 11-04-1975 |
| | | | | CA | 1083617 | ' A | 12-08-1980 |
| | | | | CA | 1092278 | 3 A | 23-12-1980 |
| | | | | CA | 1081244 | l A | 08-07-1980 |
| | | | | DE | 2448236 | 5 A | 17-04-1975 |
| | | | | FR | 2247491 | Α | 09-05-1975 |
| | | | | GB | 1490204 | A | 26-10-1977 |
| | | | | JP | 1044858 | 3 C | 30-04-1981 |
| | | | | JP | 50067400 |) A | 06-06-1975 |
| | | | | JP | 55039177 | ' B | 08-10-1980 |
| | | | | NL | 7413247 | 7 A | 15-04-1975 |
| | | | | SE | 418190 |) B | 11-05-1981 |
| | | | | SE | 7412796 | 5 A | 14-04-1975 |
| US | 4670530 | Α | 02-06-1987 | AU | 586739 | B | 20-07-1989 |
| | | | | AU | 6960387 | 7 A | 10-09-1987 |
| | | | | CA | 1282519 | 6 A | 02-04-1991 |
| | | | | EP | 0240708 | 3 A | 14-10-1987 |
| | | | | JP | 1992416 | 6 C | 22-11-1995 |
| | | | | JP | 7002907 | ' B | 18-01-1995 |
| | | | | JP | 62270660 |) A | 25-11-1987 |
| GB | 2064363 | Α | 17-06-1981 | AU | 538540 | B | 16-08-1984 |
| | | | _ | AU | 6497180 | | 11-06-1981 |
| | | | | BΕ | 886449 |) A | 02-06-1981 |
| | | | | CA | 1166549 |) A | 01-05-1984 |
| | | | | DE | 3045083 | 3 A | 19-06-1981 |
| | | | | FR | 2471210 |) A | 19-06-1981 |
| | | | | JP | 105530 | | 24-11-1989 |
| | | | | JP | 1830054 | C | 15-03-1994 |
| | | | | JP | 5609595 | 2 A | 03-08-1981 |
| | | | | SE | 800845 | : Δ | 04-06-1981 |



INTERNATIONAL SEARCH REPORT

nformation on patent family members

national Application No PCT/GB 98/00828

| Patent document cited in search repor | t | Publication date | Patent family member(s) | | | Publication date | |
|--|---|---------------------|----------------------------|----------|---|---------------------|--|
| GB 2064363 | Α | 1 | US | 4784844 | A | 15-11-1988 | |
| EP 0279641 | A | 24-08-1988 | US | 4832858 | A | 23-05-1989 | |
| 2. 02,00.0 | | • | DE | 3873375 | Α | 10-09-1992 | |
| | | | GR | 3005950 | T | 07-06-1993 | |
| | | | JP | 63225311 | Α | 20-09-1988 | |
| US 3176964 | | 06-04-1965 | NONE | | | | |

Form PCT/ISA/210 (patent family annex) (July 1992)

